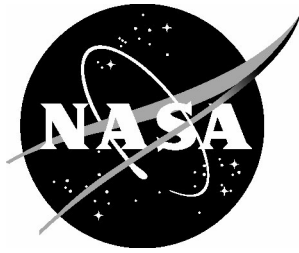# Tensile Properties of Poly (N-vinyl caprolactam) Gels

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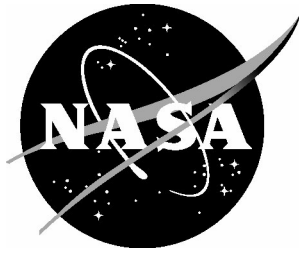
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Abstract

N-vinyl caprolactam was copolymerized with ethylene glycol dimethacrylate using a free-radical initiator in alcohol/water solution. The resulting gels were thermally-responsive in water, undergoing an approximate fivefold reversible volume shrinkage between room temperature and ca. 50 C. Tensile testing showed that the stress-strain behavior was qualitatively different in the collapsed state above the temperature-induced transition. At the higher temperature, gels were stiffer, more ductile, and showed greater time dependence. Implications for the design of gel actuators are briefly discussed.

Introduction

Stimulus-responsive hydrogels are of interest for a variety of biomedical applications [1], as microfluidic valves [2], and as actuators [3]. In spite of this widespread interest and the fact that gels can be rather fragile, measurements of strength and toughness of these materials are relatively uncommon. This memorandum describes the effect of a temperature-induced transition on the mechanical properties of a responsive poly N-vinyl caprolactam (PVCL) gel.

Experimental

N-vinyl caprolactam (Aldrich) was dissolved at 50% concentration in 80:20 (vol.) ethanol-water solution along with 1.4 mole % ethylene glycol dimethacrylate (crosslinker) and 0.5 mol % 2,2 azobis isobutyronitrile (initiator). Nitrogen was bubbled gently through the solution for 20 minutes before it was transferred to a mold consisting of two soda-lime glass plates separated by a silicone rubber gasket. Polymerization was carried out in an oven at 60 C for 4 hours. Ethanol, excess monomer and sol fraction were removed by repeatedly swelling the gel in fresh deionized water (cycling the temperature between 22 C and 55 C.) Purified gel sheets were approximately 1 mm thick at room temperature.

Samples of gel were dried to constant weight to give the mass fraction of polymer in the gel at room temperature. Temperature response of the gel was determined by blotting and weighing a small square of gel, equilibrating it at the next higher temperature, and repeating. Mass fractions were converted to volume fractions where required by assuming additivity of volumes and a polymer density of $\rho=1.23$ g/cm^3 [4].

For the mechanical testing, tapered specimens (scaled-down versions of ASTM D638 Type 5 dumbbells) were cut by hand with a razor blade with the aid of a stainless steel template. Thickness and width of each specimen were measured at room temperature using a microscope with a vernier stage and crosshair eyepiece. Dimensions are averages of 3 locations in the gauge section. Length of the straight-sided portion of the specimen was 17.75 mm at room temperature. Specimens were brought to the test temperature in a water bath, affixed to polyester film gripping tabs with cyanoacrylate adhesive and submerged during testing in a large reservoir of water at the proper temperature. Crosshead speed was 0.5 cm/min; elongation was approximated as crosshead displacement divided by the original gauge length.

Results and Discussion

Swelling characterization
The equilibrium degree of swelling at room temperature corresponds to a polymer volume fraction $\phi_2 = 0.075$. This value can be used in the Flory-Rehner equation [5] to characterize the degree of cross linking. In its usual form, the equation reads

$$V_1 n[\phi_2^{1/3} - \phi_2/2] + \ln(1-\phi_2) + \phi_2 + \chi\phi_2^2 = 0 \qquad (1)$$

In which V_1 is the solvent molar volume, n is the concentration of elastic chains, ϕ_2 is the polymer volume fraction at swelling equilibrium, and χ is the polymer-solvent interaction parameter. There are, of course, approximations inherent in the lattice-based theory itself. In addition, there are two minor problems in applying equation 1 to our gels. The first has to do with the way our material was made, and the second is uncertainty in the parameter χ that appears in the equation. Each of these will be discussed in turn.

In the Flory-Rehner derivation, the free energy of swelling consists of two terms: one due to dilution of the network chains, and one due to elastic stretching. It is reasonable to assume affine swelling [6], i.e., that the chain end-to-end distances stretch in proportion to changes in the specimen macroscopic dimensions. For a network prepared in solution, however, the reference state (where the chains are relaxed, i.e., unstretched) should be that at which crosslinking took place, not the dry state [7]. This has the effect of replacing the term in brackets in equation 1 with the expression $[(v_0/v)^{1/3} - (v_0/2v)]$, where v is the equilibrium swollen volume and v_0 is the volume at synthesis.

With regard to the χ parameter, in the context of Flory-Huggins theory

$$\chi = (1/2) - A_2 V_1 / V_2^2 \qquad (2)$$

where A_2 is the second virial coefficient and V_2 is the solute specific volume. Thus in good solvents, where $A_2 > 0$, we expect $\chi < 0.5$. The theta condition, i.e., incipient precipitation at infinite molecular weight, corresponds to $\chi = 0.5$. For PVCL in water at room temperature, small positive virial coefficients are reported [8, 9]. Furthermore, the Mark-Houwink expression [10] for the intrinsic viscosity $[\eta] = kM^a$ yields a=0.69, which would be interpreted to mean that water is a moderately good solvent. Other authors, however, back-calculate $\chi = 0.52$ [4], corresponding to a rather poor solvent, and even higher values of χ have appeared [11].

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It turns out that equation 1 is quite sensitive to the choice of χ in this range. Published virial coefficients correspond to $0.49 < \chi < 0.50$ via equation 2, so we choose $\chi = 0.5$. We can then calculate the approximate chain concentration, n, or equivalently, divide the mass concentration by the chain concentration to get the average molecular weight of a network chain, M_c. From stoichiometry, complete reaction would have resulted in $M_c \sim 5 \times 10^3$ g/mole (assuming the added cross linker formed tetrafunctional junctions.) The result calculated from the swelling experiment is $M_c = 1.1 \times 10^4$ g/mol, which is certainly the right order of magnitude. That it is higher than the stoichiometric prediction should not be too surprising. Incomplete reaction or failure to incorporate all the crosslinker (due to monomer reactivity ratios) would raise this number. Network imperfections such as loops (likely with solution cross linking) would also decrease the effective chain concentration (and therefore increase M_c).

Figure 1 illustrates how the mass of our PVCL gel at swelling equilibrium changes as a function of temperature. As the temperature is raised, the gel expels water and shrinks; the midpoint of the shrinkage transition corresponds rather closely to the lower critical solution temperature [9] of high molecular weight PVCL (approximately 31.5 C). Other workers have documented this shrinkage behavior [4,12]. At 47 C, in the shrunken state, the volume fraction of polymer was 0.372. It is commonly observed that the polymer concentration in the shrunken state of responsive gels is independent of the degree of cross linking [4,13]; thus the water content of the *shrunken* gel is determined by the polymer phase behavior, not by the chain elasticity considerations that led to equation 1.

Small-strain Moduli
Using a relationship from rubber elasticity theory, the engineering stress, σ, is given as:

$$\sigma = NRT \, (r^2/r_0^2)(\lambda - 1/\lambda^2) \qquad (3)$$

where N is the number density of elastic chains in the gel, R is the gas constant, T is the absolute temperature, and λ is the extension ratio [5]. The "front factor" (r^2/r_0^2) reflects the increase in chain dimensions in the swollen state relative to those at the synthesis concentration [7]. Assuming again that the chain end-to-end distances r scale with the sample dimensions, $(r^2/r_0^2) = (\phi_0/\phi)^{2/3}$, where ϕ_0 is the polymer volume fraction at which cross-linking took place and ϕ is the volume fraction at which tensile testing is carried out. Representative data obtained at 22 C are plotted as load against $(\lambda - 1/\lambda^2)$ in Figure 2. A total of six specimens gave an average initial slope corresponding to a modulus of 10.3 ± 2.4 kPa (average and standard deviation), which translates via equation 3 to an elastic strand molecular weight of $M_c = 7.4 \times 10^4$ g/mole.

At 47.5 C, the load-displacement behavior is qualitatively different (Figure 3). The initial (tangent) modulus is quite high, but the gel seems to exhibit a yield point at about 10% strain. There is some scatter among specimens, in part because of the uncertainty in the initial displacement, but the effect is reproducible and the load at yield (approximately 4g) is well outside the noise level of the measurement. Thus at 47.5 C, the material is acting more like a plasticized polymer than a swollen elastomer.

Larger strains

Figure 4 shows raw load-displacement data obtained at the two temperatures. The qualitative difference in behavior is apparent: at the higher temperature, we see the yield point, and a greater degree of nonlinearity in the curve. For the sake of comparison, Table I reports, in addition to initial tangent moduli, the 100%, 200%, and 300% (secant) moduli at both temperatures (all based on the initial cross-sectional areas).

Table I
Tensile properties (average and standard deviation)

Temper-ature, C	Number of speci-mens	Engineering moduli, kPa				Engi-neering failure stress, kPa	Elonga-tion at break, %
		E, (tangent)	E(100)	E(200)	E(300)		
22	6	30.1±6.6	35.6±3.9	39.6±3.3	n/a	98±13	239±26
47.5	4	940±220	54.6±8.9	45.6±4.7	47.8±5.8	830±140	500±80

Fracture

The behavior at 22 C suggests brittle fracture; i.e., the load-displacement relationship is nearly linear all the way to failure. Such fracture would be controlled by flaws that initiate cracking. At 47.5 C, the load-displacement curve is decidedly non-linear, and furthermore, it was observed that gels did not retract quickly after breaking; i.e., they show a much greater degree of viscoelasticity than the more highly swollen room temperature gel. The relatively greater ductility of the shrunken gel could therefore be the result of greater viscoelastic energy dissipation retarding crack growth. It is known that fracture in rubber is both time- and concentration-dependent [14].

For a network with uniform chain lengths, the maximum network extensibility (failure strain) would be expected to be controlled by the extensibility of the individual chains that make it up. The maximum stretch ratio of a random coil relative to the relaxed state is $x^{1/2}$, where x is the number of Kuhn segments [6]. The characteristic ratio of PVCL is not readily available, but it should be close to that of polystyrene, given their similar structures. Using this approximation, the average strand length calculated above from rubber elasticity theory would be equivalent to approximately 50 Kuhn lengths. The predicted maximum stretch of our network chains would therefore be $(50)^{1/2}$~7.

When the tensile test begins, the gel is swollen relative to the synthesis condition, so the chains are already somewhat extended at both test temperatures. In Table II we calculate the cumulative degree of stretch at failure -- that due to both swelling and tensile elongation. The shrunken gel comes fairly close to the estimated maximum stretch for random coils.

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Table II
Elongation of Network Chains

Temperature, C	Polymer Volume fraction ϕ	Linear Swelling ratio $(\phi/\phi_0)^{-1/3}$	Tensile elongation ratio	Approximate Total
(synthesis condition)	0.47	1	1	
22	0.075	2.5	2.4	4.9
47	0.372	1.1	5.0	6.1

Application

Some predictions can be made based on the average behavior summarized above. For simplicity, we shall neglect any possible time dependence; in particular, we ignore the fact that the equilibrium water content changes in response to the deformation. Consider a load-bearing application, for example in an actuator driven by the shrinkage transition. The tensile stress would have to be limited to 98 kPa (actually less than this to allow a safety factor) in order not to exceed the strength of the swollen gel at room temperature. Reading from the load/elongation curves, and allowing for the change in unstretched length, shrinkage under this load would produce a length decrease of ~60%. We note in passing that this strength and length change are somewhat lower and higher, respectively, than the corresponding values for natural muscle [15]. The mechanical work done in lifting the weight would be ~10^3 kJ (per cubic meter of dry polymer). This is considerably higher than a value reported for polyvinyl alcohol gels operating a under compressive load [16]. Other figures of merit sometimes cited for artificial muscles are power density and efficiency. The response of even 1-mm gel strips is far too slow to give muscle-like power, and changing the temperature of large gel actuators is not likely to be practical. These factors have led to an emphasis on applications of responsive gels in the forms of fine fibers and micro-scale devices.

Conclusions

Tensile testing of a responsive gel showed that the stress-strain behavior was qualitatively different in the collapsed state above the temperature-induced transition. At the higher temperature, gels were stiffer, more ductile, and showed greater time dependence.

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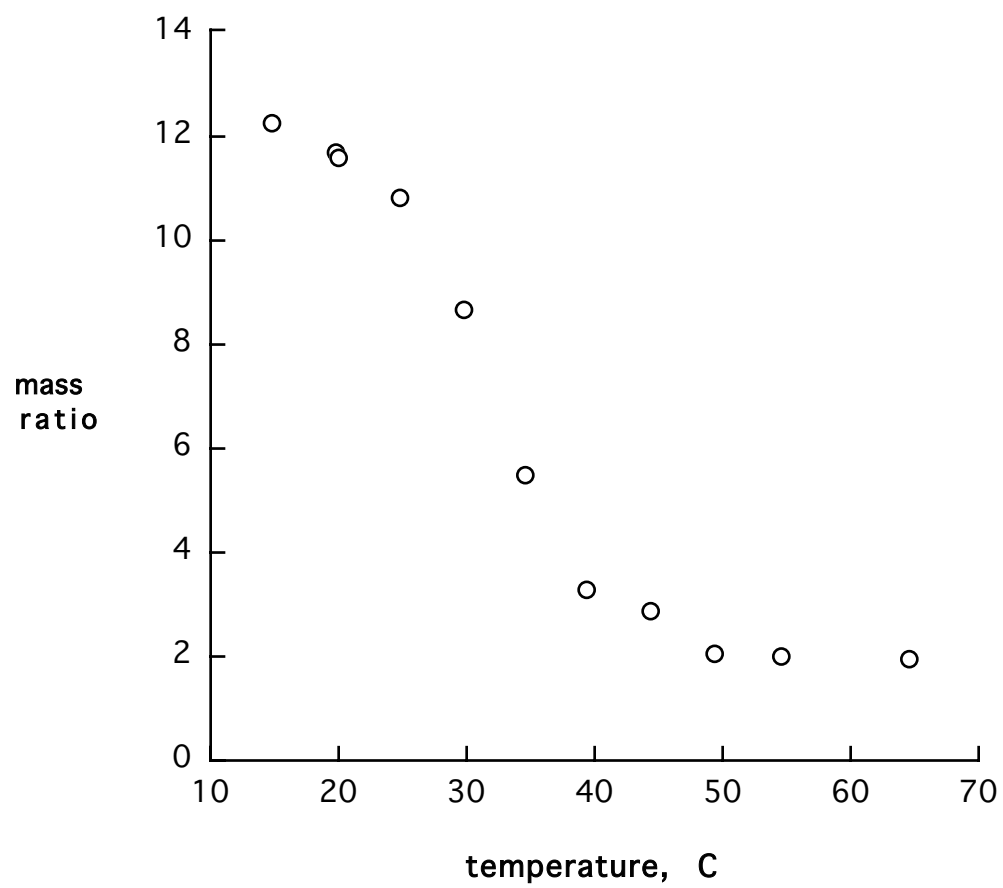
Figure 1. Degree of swelling (gel swollen weight/dry weight) vs. temperature
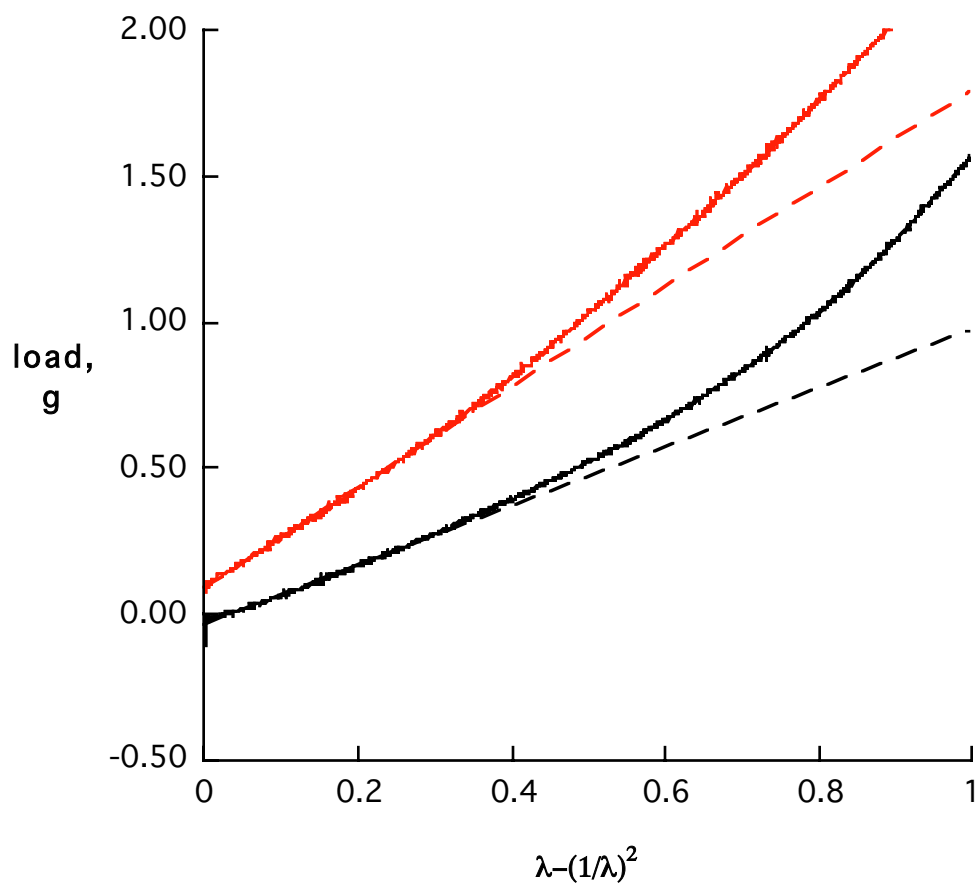
Figure 2. Tensile data at 22 C plotted according to rubber elasticity theory. Solid curves: data from two typical specimens to show degree of reproducibility. Dashed lines: least-squares fits to the region below 0.3 on the abscissa.
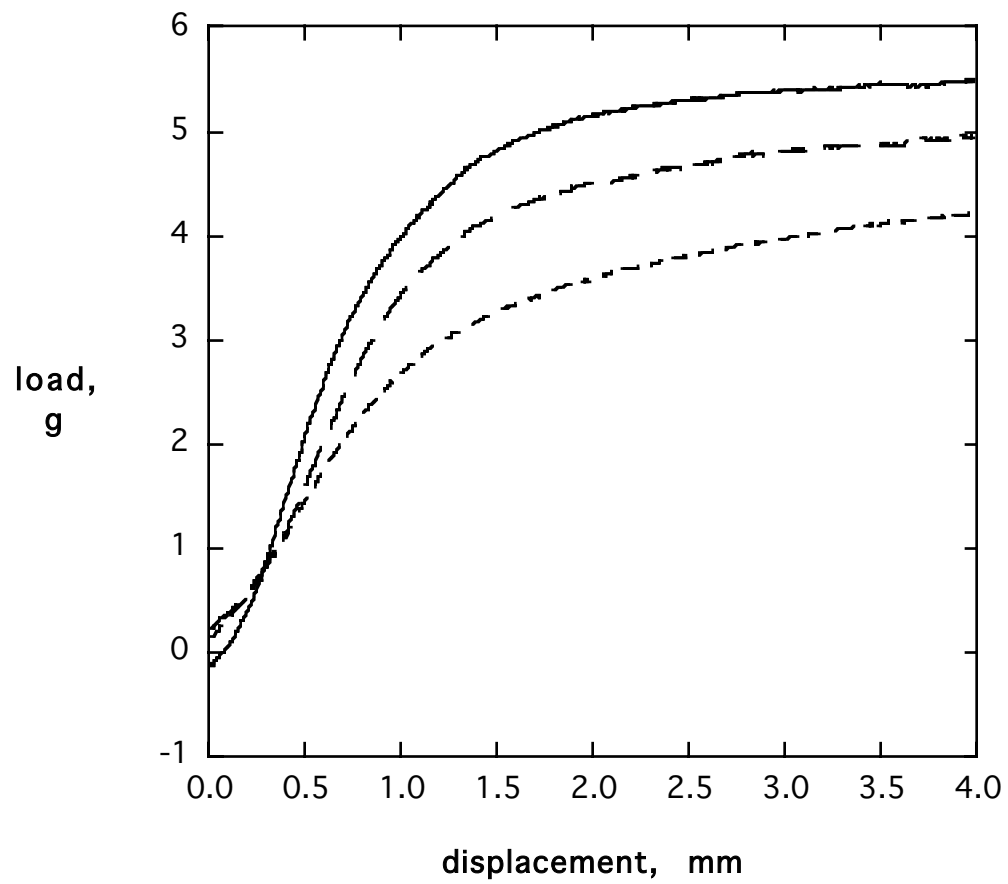
The x-axis is labeled $\lambda-(1/\lambda)^2$ and the y-axis is labeled "load, g".

Figure 3. Initial region of load-displacement curves of 3 specimens at 47 C.
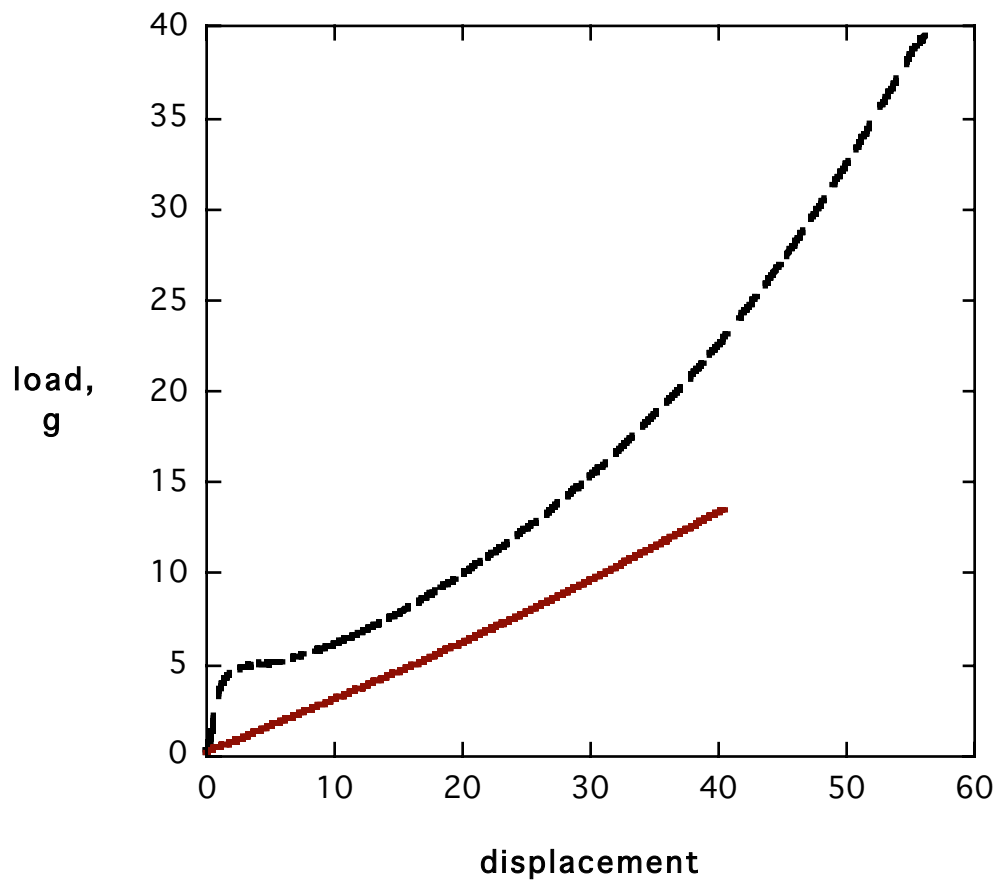
Figure 4. Complete load-displacement curves to failure at two temperatures. Solid line: 22 C.
Dashed line: 47 C.

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14. ABSTRACT

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